6258 *Organometallics* **2007,** *26,* 6258−6262

Remarkable Dichotomy of Oligomeric Chain Structures of Dilithium(amidoalkyl-cyclopentadienide) Systems $Li_2[C_5H_4\text{-CHR-NAr}]$

Vasily V. Kotov, Cun Wang, Gerald Kehr, Roland Fröhlich, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

Received September 4, 2007

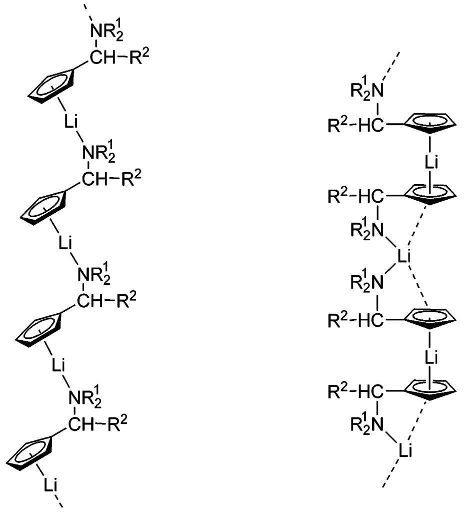
The dilithium compounds $Li_2[Cp\text{-}CHR^1\text{-}NAr^1]$ **2A** (R^1 = *tert*-butyl, Ar^1 = *p*-anisyl) and $Li_2[Cp\text{-}CHR^2\text{-}NAr^2]$ **2B** (R^2 = methyl, Ar^2 = *o*-anisyl) were synthesized by means of fulvene routes as previously described. Single crystals were obtained from THF/pentane. Both systems feature oligomeric chain structures in the solid state. Compound **2A** exhibits a head-to-tail arrangement of monomeric units with recurring chain-constructing (amide)N-Li-(η^5-Cp) units whereas **2B** favors a head-to-head type structure with alternating η^5-Cp-Li-η^5-Cp lithiocene and bis(N,O-chelate)Li building blocks. In each case the remaining Li^+ ions are coordinated toward the periphery of the main chain as $Li(THF)_2$ (**2A**) or Li(THF) (**2B**) solvates.

Introduction

The alkali metal cyclopentadienides can feature a variety of structural types, ranging from ligand-stabilized monomers through anionic metallocene-like structures all the way to the oligomeric supersandwich chain structures.[1−3] We have recently shown that Li-cyclopentadienides (**1**) that bear substituted $-CHR\text{-}NMe_2$ side chains at the Cp ring may feature one of two limiting oligomeric structural types in the solid state, namely a head-to-tail arrangement (**1A**), where both the Cp and the $-NMe_2$ donor coordination to Li^+ repetitively build up the chain, and the head-to-head alternative (**1B**) where alternating lithiocene anion/bis(amino)Li^+ cation moieties form the recurring units of the oligomeric chain (see Scheme 1).[4,5] This structural dichotomy between these alternatives seems to be more general than previously thought.

We had previously described the $(Cp\text{-}CHR^1\text{-}NR^2)MX_2$ class of compounds (M = Group 4 metal),[6−8] the C_1-bridged analogues of the ubiquitous silylene-bridged "constrained geometry" homogeneous Ziegler−Natta catalyst precursors.[9−10] These were synthesized by reaction sequences that involved transmetallation of the respective $Li_2[Cp\text{-}CHR^1\text{-}NR]$ reagents

Scheme 1



1A **1B**

---

[1] Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217−295. Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1−17. Weiss, E. *Angew. Chem.* **1993**, *105*, 1565−1587; *Angew. Chem., Int. Ed.* **1993**, *32*, 1501−1523. Stalke, D. *Angew. Chem.* **1994**, *106*, 2256−2259; *Angew. Chem., Int. Ed.* **1994**, *33*, 2168−2171. Harder, S. *Coord. Chem. Rev.* **1998**, *176*, 17−66. Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969−990. Jutzi, P.; Reumann, G. *J. Chem. Soc., Dalton Trans.* **2000**, 2237−2244.

[2] Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühlm, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776−8789. Paradies, J.; Erker, G.; Fröhlich, R. *Angew. Chem.* **2006**, *118*, 3150−3153; *Angew. Chem., Int. Ed.* **2006**, *45*, 3079−3082.

[3] Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903−3907. Könemann, M.; Erker, G.; Fröhlich, R.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1997**, *119*, 11155−11164. Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855−3858. Dinnebier, R. E.; Schneider, M.; van Smaalen, S.; Olbrich, F.; Behrens, U. *Acta Crystallogr., Sect. B* **1999**, *55*, 35−44. Dinnebier, R. E.; Neander, S.; Behrens, U.; Olbrich, F. *Organometallics* **1999**, *18*, 2915−2918. Fauré, J.-L.; Erker, G.; Fröhlich, R.; Bergander, K. *Eur. J. Inorg. Chem.* **2000**, 2603−2606. Kotov, V. V.; Kehr, G.; Fröhlich, R.; Erker, G. *Z. Naturforsch.* **2006**, *61b*, 1319−1322.

[4] Kunz, K.; Pflug, J.; Bertuleit, A.; Fröhlich, R.; Wegelius, E.; Erker, G.; Würthwein, E.-U. *Organometallics* **2000**, *19*, 4208−4216.

[5] For remotely related systems see e.g.: Könemann, M.; Erker, G.; Grehl, M.; Fröhlich, R.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1995**, *117*, 11215−11219.

[6] Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24*, 4760−4773.

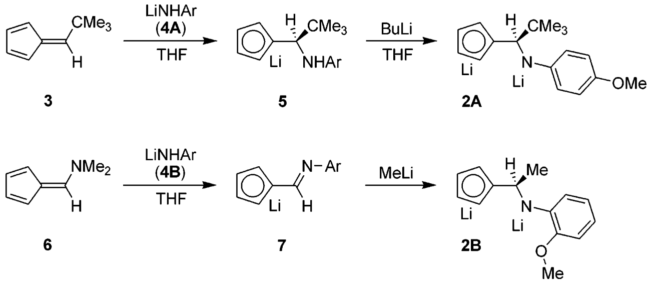
[7] Duda, L.; Erker, G.; Fröhlich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1153−1162. Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181−6182. Kunz, K.; Erker, G.; Döring, S.; Bredeau, S.; Kehr, G.; Fröhlich, R. *Organometallics* **2002**, *21*, 1031−1041.

[8] See also: Kunz, K.; Erker, G.; Kehr, G.; Fröhlich, R.; Jacobsen, H.; Berke, H.; Blacque, O. *J. Am. Chem. Soc.* **2002**, *124*, 3316−3326. Altenhoff, G.; Bredeau, S.; Erker, G.; Kehr, G.; Kataeva, O.; Fröhlich, R. *Organometallics* **2002**, *21*, 4084−4089. Bredeau, S.; Altenhoff, G.; Kunz, K.; Döring, S.; Grimme, S.; Kehr, G.; Erker, G. *Organometallics* **2004**, *23*, 1836−1844.

[9] Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74−84. Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. Okuda, J. *J. Chem. Ber.* **1990**, *123*, 1649−1651. Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132−3134. Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 2938−2953 and references cited therein.

10.1021/om700885g CCC: $37.00

Scheme 2



(**2**) to selected Group 4 transition metal complexes as an essential step. We were now able to obtain single crystals of two representative examples (**2A**, **2B**) of such dilithium Cp-amidoalkyl systems that allowed the determination of their preferred oligomeric chain structures in the solid state. As expected, both have involved binding of the lithium$^+$ cations to both the cyclopentadienide[1−3] and the amide anion moieties,[11] but in markedly different ways. These two selected structural alternatives showed remarkable similarities to the essential bonding features that have characterized the head-to-tail (**1A**) and head-to-head (**1B**) alternatives that were previously observed for the related Li[Cp-CHR^1-NR$^2_2$] systems (see above). It now appears that this structural dichotomy seems to be rather frequently encountered in (M$^+$)$_n$(Cp-X-Y)$^{n-}$ situations. Details of the representative structures of the systems **2A** and **2B** are described below.

Discussion

Synthesis of the Li$_2$[Cp-CHR^1-NR] Systems. Compounds **2** were synthesized as previously described by us.[6] The compounds **2A** and **2B** were prepared by different variants of fulvene routes.[12] Treatment of 6-*tert*-butylpentafulvene (**3**)[13] with lithium *p*-methoxyanilide (**4A**) gave the addition product (**5**), which represents a functionalized lithium cyclopentadienide. Deprotonation at the pendant secondary amino substituent was carried out by subsequent reaction with *n*-butyl lithium to yield **2A** (see Scheme 2). Under the specifically applied reaction conditions, the system **2A** was isolated as a microcrystalline solid that contained THF. Crystallization of this material from a THF/pentane mixture eventually gave the single crystals that were used for the X-ray crystal structure analysis of **2A**.

Compound **2B** was prepared starting from 6-dimethylaminopentafulvene (**6**).[14] Addition of *o*-methoxyanilide led to exchange of the amino groups with HNMe$_2$ elimination[15] to yield the aldimino-substituted cyclopentadienide (**7**). Subsequent methyl lithium addition then gave **2B**. Single crystals of **2B** were also obtained from THF/pentane solution.

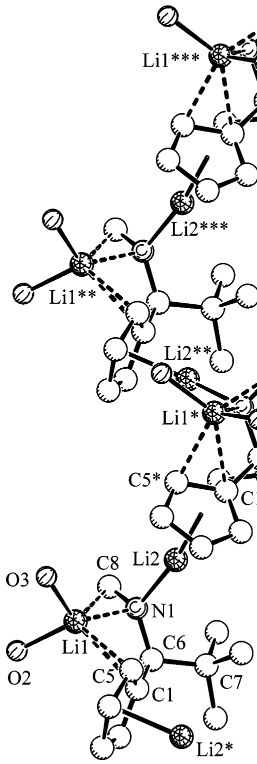
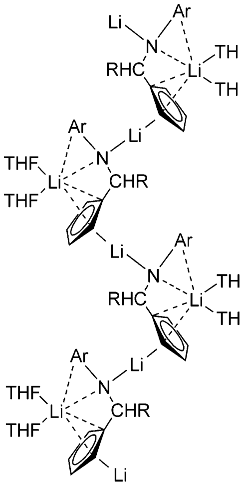


Figure 1. A view of the head-to-tail arrangement of the oligomeric chain structure of compound **2A** (*p*-methoxyphenyl group at nitrogen and thf ligands at Li(1) omitted for clarity).

Scheme 3



2A

Oligomeric Chain Structures of 2A and 2B in the Crystal. Compound **2A** features a head-to-tail arrangement of [Cp-CHCMe$_3$-NAr]$^{2-}$ building blocks along an oligomeric chain. The organometallic main chain of **2A** is composed of individual [Cp-CHCMe$_3$-NAr]$^{2-}$ moieties that are each connected by a single Li$^+$ cation. This Li(2) ion is close to symmetrically η^5-coordinated to the Cp-ring of one ligand [Li(2)−C(Cp) ranging from 2.207(4) to 2.401(4) Å] and the amide nitrogen center of the next neighboring ligand [Li(2)−N1 1.998(4) Å, angle N1−Li(2)−Cp(centroid) 166.0°]. This arrangement leads to an

---

(10) Reviews: McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598. Okuda, J.; Eberle, T. Half-Sandwich Complexes as Metallocene Analogues. In *Metallocenes-Synthesis, Reactivity, Applications*; Togni, A., Haltermann, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, pp 415−453. Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691−2720.

(11) Selected examples: Aubrecht, K. B.; Lucht, B. L.; Collum, D. B. *Organometallics* **1999**, *18*, 2981−2987. Armstrong, D. R.; Carstairs, A.; Henderson, K. W. *Organometallics* **1999**, *18*, 3589−3596. Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc*. **1999**, *121*, 10198−10202. van Vliet, G. L. J.; Luitjes, H.; Schakel, M.; Klumpp, G. W. *Angew. Chem.* **2000**, *112*, 1707−1709; *Angew. Chem., Int. Ed.* **2000**, *39*, 1643−1645.

(12) Reviews: Bertuleit, A.; Könemann, M.; Duda, L.; Erker, G.; Fröhlich, R. *Top. Catal.* **1999**, *7*, 37−44. Erker, G. *Coord. Chem. Rev.* **2006**, *250*, 1056−1070.

(13) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849−1853.

(14) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Liebigs Ann. Chem.* **1961**, *641*, 1−39. Hafner, K.; Schulz, G.; Wagner, A. *Liebigs Ann. Chem.* **1964**, *678*, 39−53. Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Org. Synth.* **1967**, *47*, 52−54.

(15) Kunz, K.; Erker, G.; Kehr, G.; Fröhlich, R. *Organometallics* **2001**, *20*, 392−400 and references cited therein.

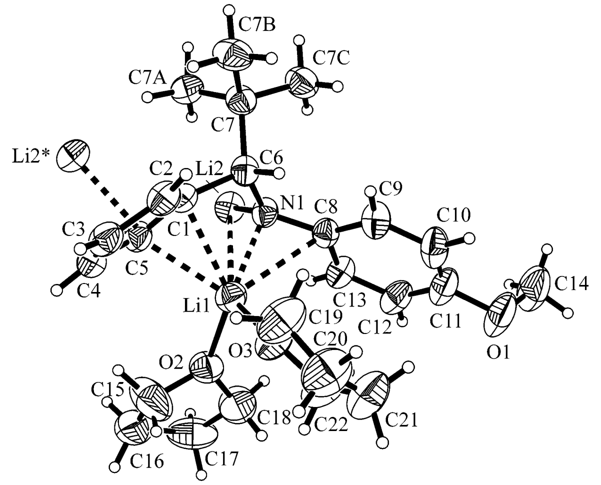


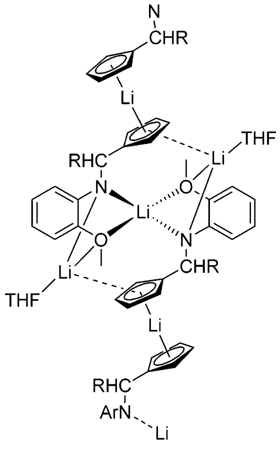
Figure 2. A view of the detailed coordination geometry of the asymmetric subunit of **2A** whose repetition makes up the oligomeric chain structure of this compound.

oligomeric zigzag chain with recurring [Cp-CHCMe$_3$-NAr]$^{2-}$-Li$^+$ subunits (see Figure 1 and Scheme 3).

The other lithium ion [Li(1)] does not actively participate in the formation of the oligomeric chain of **2A**. It is η^2-coordinated at the Cp-ring [Li(1)−C(5) 2.353(4) Å, Li(1)−C(1) 2.499(4) Å, angles Li(1)−C(1)−C(5) 67.4(1)°, Li(1)−C(5)−C(1) 78.7(1)°] oriented opposite to Li(2*). This places this lithium cation Li(1) at the periphery of the main chain structure. Li(1) is stabilized by coordination of a pair of THF ligands [Li(1)−O(3) 1.961(4) Å, Li(1)−O(2) 1.971(4) Å, angle O(3)−Li(1)−O(2) 101.2(2)°] and by coordination to N(1) [Li(1)−N(1) 2.088(4) Å]. In addition, Li(1) seems to have a weak bonding interaction with the ipso-carbon atom of the electron-rich *p*-methoxyphenyl substituent at the amide nitrogen [Li(1)−C(8) 2.570(4) Å]. This interaction may lead to some “stiffening” of the oligomeric chain structure (see Figure 2).

The oligomeric chain structure of compound **2B** is of the head-to-head type (see Figure 3 and Scheme 4). It can be seen that the main chain is composed of lithiocene anion substructures and (bis-O,N-chelat)Li$^+$ cation moieties that follow each other in a strictly alternating pattern. Additional Li$^+$ cations [Li(3)] are attached to each of the individual O,N-chelate moieties. They are oriented toward the periphery of the chain structure and each of the Li(3) atoms has a stabilizing THF ligand coordinated to it. Consequently, the structure of **2B** features the peculiarity that it is composed of [Cp-CHMe-NAr]Li$_2$ subunits but clearly exhibits three different types of lithium ions. This is only a strange behavior at first sight, since both the chain constructing lithium atoms Li(1) and Li(2) share pairs of [Cp-CHMe-NAr] ligands between them, so, formally they bear only a 50% weight relative to their attached monomeric moieties. Only the peripheral Li(3) atom fully belongs to its individual [Cp-CHMe-NAr] subunit.

Scheme 4



2B

Lithium atom Li(1) in **2B** occupies the center of a near to perfect lithiocene anion structure. The two Cp-rings are symmetry equivalent. The Li(1)−C(1) to C(5) distances were found in a narrow range between 2.278(2) [Li(1)−C(4)] and 2.323(2) Å [Li(1)−C(2)]. The adjacent Li(2) atom is symmetrically coordinated to the pair of O,N-chelate ligands comprised of the *o*-methoxyanilide substituents [Li(2)−N(1) 1.948(2) Å, Li(2)−O(1) 2.030(3) Å]. In addition we note a pair of short Li(2)−C(arene) contacts [Li(2)−C(8) 2.646(2) Å, Li(2)−C(13) 2.721(3) Å] which are probably just spatially enforced, and a rather short Li(2)−Li(3) separation [2.664(3) Å].

Li(3) is much less strongly bonded to the O,N-chelate [Li(3)−O(1) 2.544(3) Å, Li(3)−N(1) 2.084(3) Å]. It has a THF ligand tightly bonded [Li(3)−O(2) 2.012(3) Å] and Li(3) features rather unsymmetrical contact to the next lithiocene Cp-ring (opposite to Li(1)#2) [Li(3)−C(4)#2 2.334(3) Å, Li(3)−C(3)#2 2.420(3) Å, Li(3)−C(5)#2 2.540(3) Å, Li(3)−C(2)#2

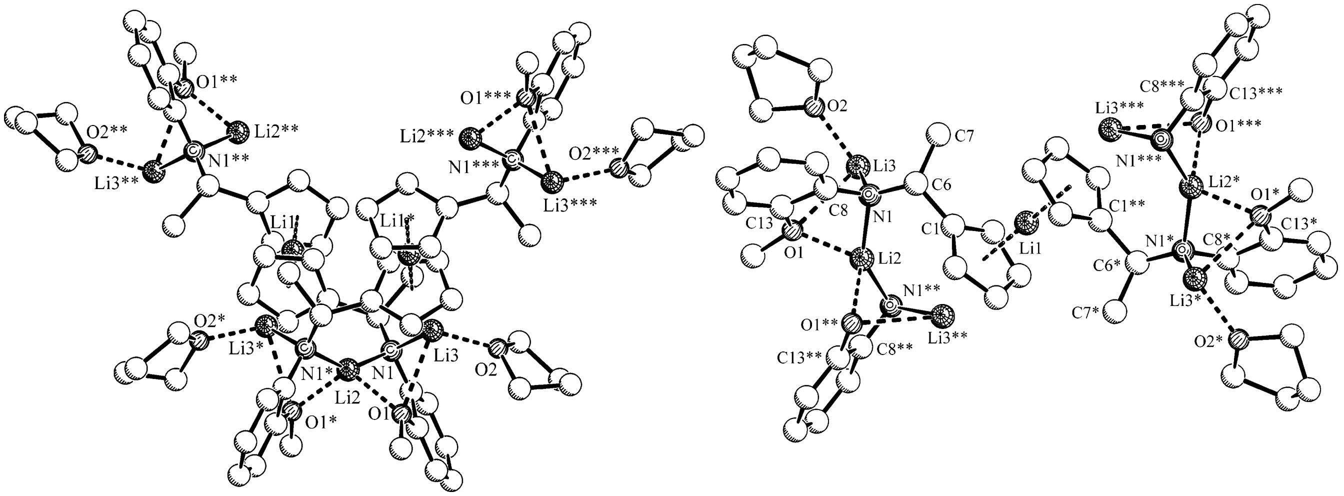


Figure 3. Two projections of the head-to-head oligomeric chain structure of **2B** featuring alternating lithiocene anion/chelate-Li$^+$ cation moieties.

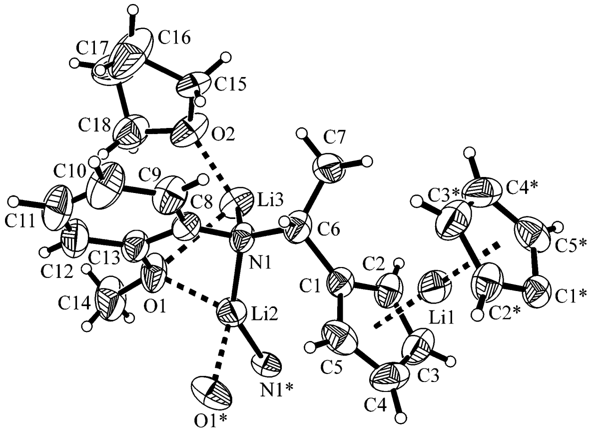


Figure 4. A view of the recurring building block of the oligomeric chain of **2B** [Li(1) and Li(2) bear only 50% weight relative to the monomeric unit].

2.659(3) Å, Li(3)−C(1)#2 2.754(3) Å]. There is also a short Li(3)−C(8) arene contact of 2.772(3) Å.

Conclusions

In their detail the oligomeric chain structures of the Li_2[Cp-CHR-NAr] compounds **2A** and **2B** appear rather complicated, but it seems that in their essence they closely resemble the head-to-tail (**1A**) and head-to-head (**1B**) structural types that were previously observed for the lithium compounds of the monoanionic ligand types [Cp-CHR′-NR$_2$]$^-$. In **2A** we observe a symmetrical recurring of the monomeric dianionic [Cp-CHR-NAr]$^{2-}$ ligand with a connecting Li$^+$ oriented between an amide nitrogen of one unit with a Cp-coordination of the next unit. A schematic representation of this characteristic bonding type is depicted in Figure 5 (left drawing). It seems that the coordination of the second Li$^+$ ion in a way is akin to a mere decoration at the periphery, although its involvement in the overall structural outline probably provides additional stabilization of the framework aside from the necessary charge compensation.

Compound **2B** shows a fundamentally different structure. Here a head-to-head arrangement of ligands is observed. This results in the formation of a close to ideal lithiocene anion building block, in which both cyclopentadienides share a single Li$^+$ in a twofold η^5-coordination. Its opposite Li$^+$ site principally features lithium in a twofold O,N-chelate situation, with both O,N donors again coming from different individual ligand entities (see Figure 5, right). The remaining Li$^+$ cation that is necessary for charge compensation seems to play a supporting role in this overall "**B**-type" structural arrangement.

It seems that the lithium Cp-alkylamino and Cp-alkylamido derivatives have a choice of forming favored organometallic oligomeric chain structures by predominantly Coulombic interactions[16] that feature head-to-tail (**A**) or head-to-head (**B**) ligand arrangements regardless of the formal ligand charge. It seems that the specifically favored variant in each case is determined by the nature (and probably the steric properties) of the alkyl substituent at the bridging carbon atom. It may therefore be that such systems might turn out to be suited test cases for future attempts to a priori predicting of favored solid-state structures from a limited selection of alternatives.

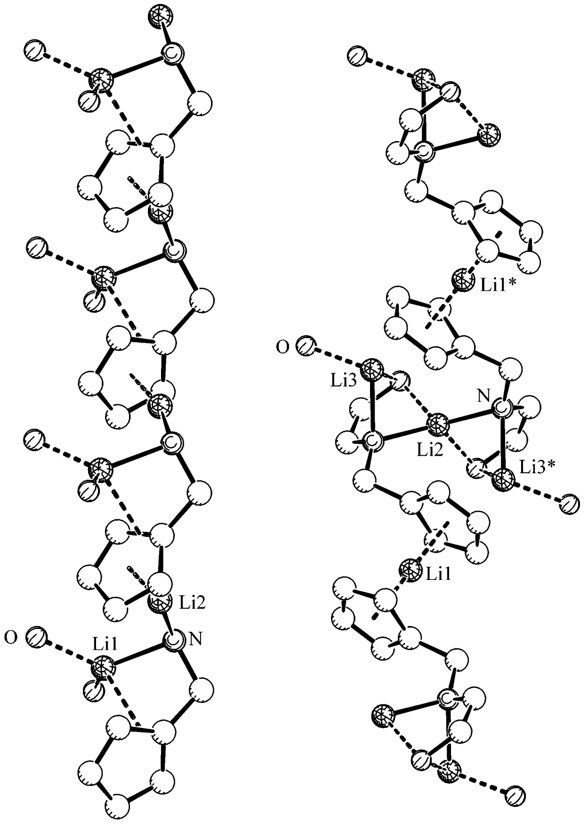


Figure 5. Schematic representation of the different coordination modes characterizing the oligomeric organometallic chain structures of compounds **2A** (left, head-to-tail) and **2B** (right, head-to-head).

Experimental Section

General Information. All reactions with organometallic reagents or substrates were carried out under argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instrument was used for spectroscopic characterization of the compounds: Bruker AMX 400 NMR spectrometer. Compounds **2A** and **2B** were prepared by procedures closely related to those published by us recently.[6] Single crystals of these compounds were obtained from THF/pentane by the diffusion method.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, ref 17), absorption correction Denzo (Otwinowski et al., ref 18), structure solution SHELXS-97 (Sheldrick, ref 19), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997), and graphics XP (BrukerAXS, 2000).

Preparation of Compound 2B. Lithium *o*-methoxyanilide (41.3 mmol) was prepared by adding *n*-BuLi (1.74 M in hexane, 30.0 mL, 30.0 mmol) to a solution of *o*-anisidine (3.69 g, 30.0 mmol) in 20 mL of THF at −78 °C. The reaction mixture was stirred at room temperature for 1 h. The solution of the lithium anilide was added slowly to a solution of 6-(dimethylamino)fulvene (3.63 g, 30.0 mmol) in 20 mL of THF, and the reaction mixture was stirred overnight. The reaction mixture was concentrated under vacuum to near dryness, and then 50 mL of ether was added. At −78 °C,

---

(16) Sapse, A.-M.; Schleyer, P. v. R., Eds. *Lithium Chemistry*: *A Theoretical and Experimental Overview*; Wiley: New York, 1995. Review: Budzelaar, P. M.; Engelberts, J. J.; van Lenthe, J. H. *Organometallics* **2003**, *22*, 1562−1576.

(17) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.

(18) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor,W. *Acta Crystallogr.* **2003**, *A59*, 228−234.

(19) Sheldrick,G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

MeLi (2.04 M in ether, 14.7 mL, 30.0 mmol) was added slowly, and the reaction mixture was stirred overnight. All volatiles were removed under vacuum. The residue was washed with pentane and dried under vacuum to give a brown powder. Isolated yield: 8.31 g (29.0 mmol, 97%).

Anal. Calcd for $C_{14}H_{15}ONLi_2 \cdot (C_4H_8O)$: C 72.24, H 7.75, N 4.68. Found: C 71.63, H 7.71, N 4.52. ^1H NMR (d_8-THF, 400 MHz, 300 K) δ 6.45, 6.29, 6.12, 5.56 (ABCD, each 1H, C_6H_4OMe), 5.99, 5.53 (m, each 2H, Cp), 4.27 (br, 1H, Cp-C*H*), 3.63 (s, 3H, OCH_3), 1.32 (br. d, 3H, CH_3).

X-ray crystal structure analysis of **2B**: formula $C_{18}H_{23}Li_2NO_2$, $M = 299.25$, colorless crystal $0.35 \times 0.15 \times 0.10$ mm^3, $a = 24.270(1)$ Å, $b = 9.386(1)$ Å, $c = 16.451(1)$ Å, $\beta = 113.87(1)°$, $V = 3427.0(4)$ Å,^{3} $\rho_{calcd} = 1.160$ g cm^{-3}, $\mu = 0.566$ mm^{-1}, empirical absorption correction ($0.826 \leq T \leq 0.946$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 20799 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 3027 independent ($R_{int} = 0.046$) and 2670 observed reflections [$I \geq 2\sigma(I)$], 249 refined parameters, $R = 0.049$, $wR^2 = 0.133$, max. residual electron density 0.27 (−0.16) e Å^{-3}, THF solvent molecule refined with split positions, hydrogen atoms calculated and refined as riding atoms.

Preparation of Compound 2A. Analogously as described above lithium *p*-methoxyanilide (3.69 g, 30.0 mmol) was reacted with 6-*tert*-butylpentafulvene (4.02 g, 30.2 mmol) to give compound **2A** as a yellow solid (8.83 g, 91%).

Anal. Calcd for $C_{17}H_{21}ONLi_2 \cdot 2(C_4H_8O)$: C 72.63, H 9.02, N 3.39. Found: C 71.48, H 8.67, N 3.42. ^1H NMR (d_8-THF, 400 MHz, 300 K) δ 6.28, 5.62 (AA′BB′, each 2H, C_6H_4OMe), 5.97, 5.62 (br, each 2H, Cp), 3.99 (br, 1H, Cp-C*H*), 3.47 (s, 3H, OCH_3), 0.97 (s, 9H, $C(CH_3)_3$).

X-ray crystal structure analysis of **2A**: formula $C_{25}H_{37}Li_2NO_3$, $M = 413.44$, red crystal $0.35 \times 0.20 \times 0.15$ mm^3, $a = 12.293(1)$ Å, $b = 19.924(1)$ Å, $c = 10.208(1)$ Å, $\beta = 107.19(1)°$, $V = 2388.5(3)$ Å,^{3} $\rho_{calcd} = 1.150$ g cm^{-3}, $\mu = 0.564$ mm^{-1}, empirical absorption correction ($0.827 \leq T \leq 0.920$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 16084 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 4179 independent ($R_{int} = 0.041$) and 3591 observed reflections [$I \geq 2\sigma(I)$], 284 refined parameters, $R = 0.060$, $wR^2 = 0.158$, max. residual electron density 0.36 (−0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. V.V.K. thanks the Alexander von Humboldt Foundation for a stipend.

Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700885G